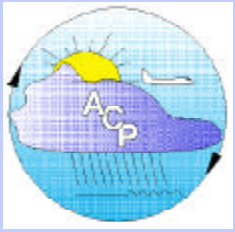


Aerosol Chemistry in the Nighttime Boundary Layer

an integrated laboratory, field and modeling study

Pacific Northwest National Laboratory * • *Battelle Columbus Laboratory* • *Argonne National Laboratory*

The Problem: Model predictions of HNO_3 /NO_X in remote atmospheres are overestimated by a factor of 5-10 compared to measurements, even though ozone mixing ratios are adequately simulated. This implies that air quality models may be predicting the right answers for the wrong reasons.

Hypothesis: a) Heterogeneous reactions of NO_Y species on the surface of aerosols play an important role in the distribution of NO_Y, O_3 and other oxidants. b) These reactions may explain the discrepancy between observations and models. c) NO_X is regenerated from HNO_3 + aerosol reactions. d) These reactions are most significant at night, in the absence of competing photochemical processes and when turbulent mixing is at a minimum.

Jim Cowin (PNNL) and Rob Disselkamp (PNNL)

Laboratory Questions:

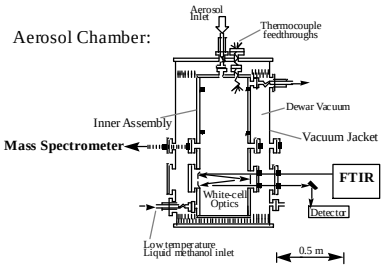
What are the key nitrogen reactions to occur on the surfaces of carbonaceous aerosols? How long do they occur under various conditions? What are the kinetics behind these reactions?

Approach:

a) Quantitatively measure gaseous products resulting from aerosol surface reactions by directing trace gases onto carbonaceous aerosols, followed by analysis of products.

Real Aerosols

Aerosol Chamber:



1. Temperature controlled from 300 to 185 K.
2. Teflon coated inner surfaces.

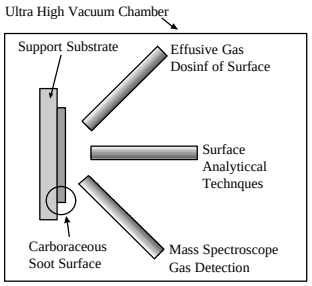
***Experimental Procedure**

1. Introduce Reactant gases into Chamber - characterize with IR/MS
2. Add Aerosol sample (Carbonaceous soot, Sea-Salt, etc.)
3. Monitor reactant gas change over time (> 100 minutes)
4. Extract particles onto filter material for elemental/ structural characterization (XPS, STM, AFM)

***Project Goals**

1. Obtain heterogeneous reaction efficiencies for use in atmospheric models.
2. Idnetify interaction among trace gas species of atmospheric interest.
3. Elucidate chemical mechanisms/rate processes.

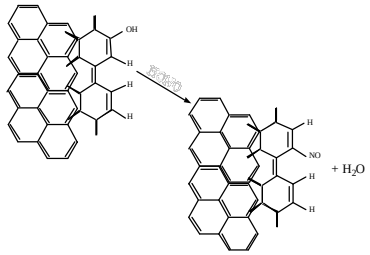
UHV Appartus/Imagine Reactions at Surfaces



Description of Analystical Techniques:

- STM (Scanning Tunneling Microscopy)
- HREELS (High Resolution Electron Energy Loss Spectroscopy)
- IRAS (Infrared Reflection A

Example of Fundamental Soot Chemistry



b) Tag reactant molecules to help trace reactions mechanisms using ultrahigh vacuum surface kinetics apparatus

c) Evaluate time during which aerosol surface reactions can occur (all night? a few hours?) using scanning tunneling microscope.

Expected Results:

a) Empirical functions relating aerosol surface reactions to ambient conditions, e.g.
.$\partial[NOx]/\partial t = \beta(\text{moisture, temperature, } O_3,...)[HNO_3]$, suitable for inclusion in atmospheric models of lower tropospheric chemistry and transport.

b) Elucidation of the kinetics behind these empirical functions.

c) Explicit descriptions of aerosol surface reactions under various ambient conditions, e.g., $HNO_3 + \text{aerosol} \overset{k}{\Rightarrow} NO$, suitable for inclusion in atmospheric models of lower tropospheric chemistry and transport.

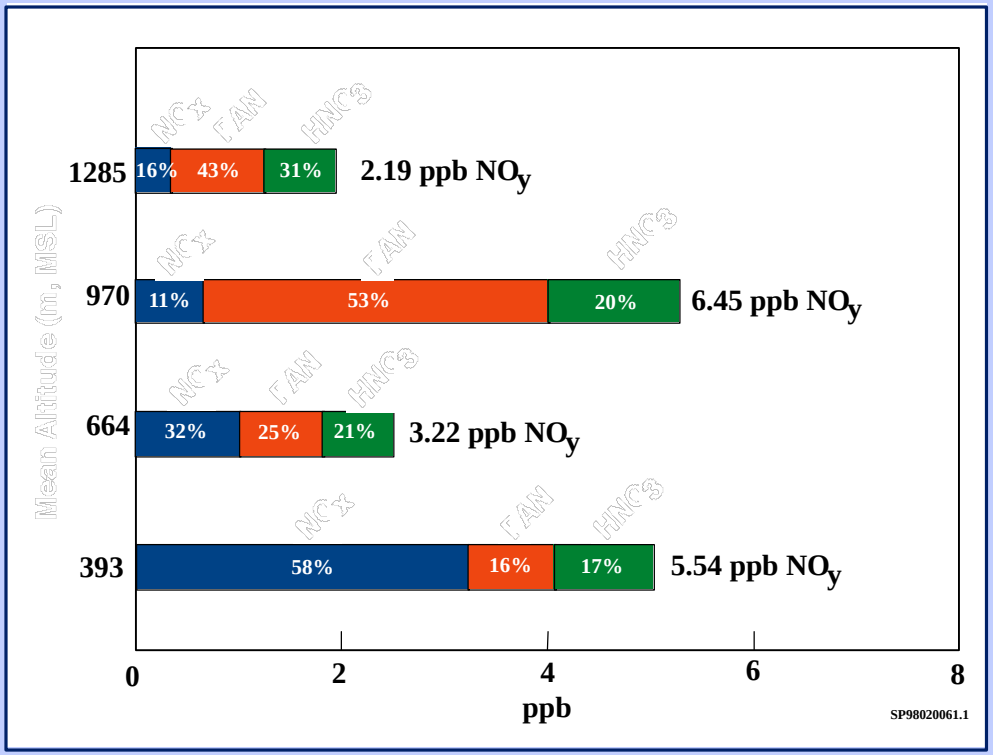
Chet Spicer (BCL) and Carl Berkowitz *(PNNL)

Field Questions:

What is the gas-phase and aerosol environment in which these reactions occur? How does the chemical speciation of NO_y change during the night?

Approach:

a) Provide vertical profiles of speciated NO_y and related gas-phase species at night using API-365 MS/MS for HNO_3 and HONO (few nocturnal observations of these quantities above the nocturnal stable layer are available).



The chemical speciation of NO_y as a function of attitude, based on measurement taken by the DOE G-1 research aircraft during the NARSTO '95 field campaign. Similar measurements, augmented with aerosol size and compositions, are planned for the field component of the Nighttime Chemistry Study.

b) Concurrent aerosol and hydrocarbon observations.

c) Empirical analysis relating aerosol profiles to oxidant levels using statistics and chemical box-model analysis.

Expected Results:

a) A unique data set for use in model evaluations by a variety of atmospheric chemists and modelers.
b) Base case for analysis by the modeling component of this study.
c) Establishment of new airborne measurement capability for ACP scientists and other atmospheric chemists.

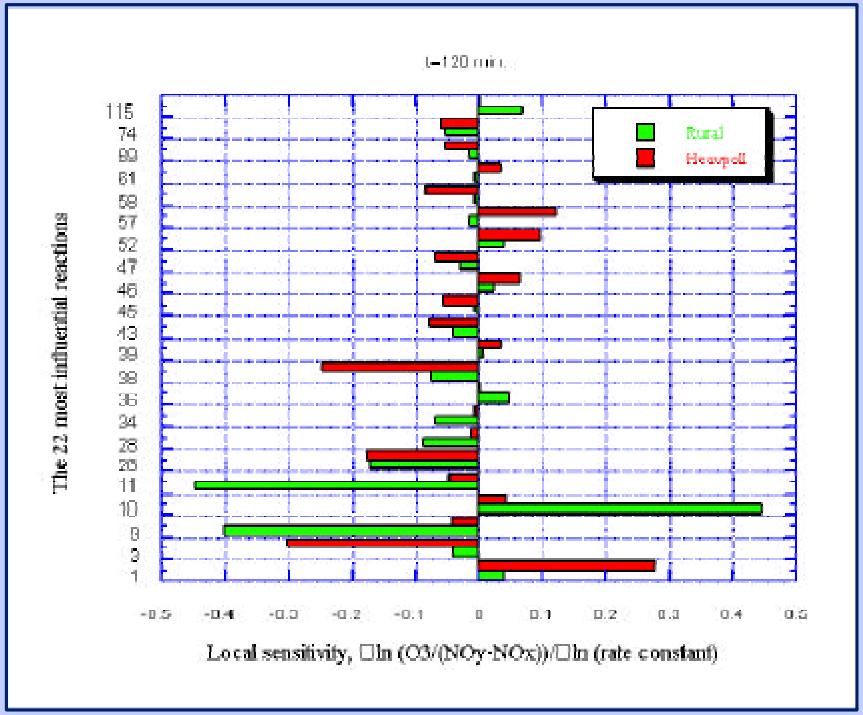
*Chris Bischof (ANL) and Carl Berkowitz *(PNNL)*

Modeling Questions:

How important are aerosol surface reactions relative to other processes of known significance to peak oxidant levels? What is the relative importance of aerosol reactions relative to mixing? To the thermal structure of the atmosphere?

Approach:

a) Apply automated differentiation (AD) tools to coupled RAMS/GChM atmospheric chemistry/transport model.



The above figure illustrates the use of automated differentiation to produce a series of sensitivity coefficients. In this example, the 22 most influential reactions associated with the so called "indicator species", $O_3/[NO_Y - NO_X]$, are shown for initial conditions associated with both a rural and heavily polluted environment. A similar analysis will include meteorological and aerosol processes.

b) Use AD to assess roles of existing gas-phase chemistry, mixing, temperature stratification, etc.

c) Incorporate laboratory results into RAMS/GChM

d) Use RAMS/GChM to simulate field observations

Expected Results:

a) Sensitivity analysis for existing coupled RAMS/GChM modeling system
b) Simulation of field observations, specifying aerosol size and composition, calculating NO_y speciation (NO_y, NO_x, NO_3^-,...)
c) Sensitivity analysis of refined RAMS/GChM system, using laboratory derived chemical kinetics (see left) to evaluate magnitude of sensitivity coefficients for aerosol surface reactions relative to other coefficients from AD/model simulations.

Lead Laboratory, Principal Investigator